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An XPS and Electrochemical Study of the Influence of
Molybdenum and Nitrogen on the Passivity of Austenitic Stainless
Steel

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AN XPS AND ELECTROCHEMICAL STUDY OF THE INFLUENCE OF MOLYBDENUM AND NITROGEN ON THE PASSIVITY OF AUSTENITIC STAINLESS STEEL

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ABSTRACT

In previous surface studies of N bearing stainless steels exposed to acidic environments we have determined that N is anodically segregated as a surface nitride phase. In this paper we have focused on the nature of the surface nitride and its role in the passivity of each of the constituent elements comprising a Mo bearing stainless steel.

To facilitate this study, surface nitrides were generated electrochemically at room temperature on the surface of high purity samples of Cr, Mo, Fe and Ni and on the surface of types 304, 317LX, 904L and AL6X stainless steels. The effect of the surface nitriding treatment on the anodic kinetics of the stainless steels was in close agreement with the effect of N alloying. The surface nitriding of Cr resulted in the complete elimination of the active nose in deaerated 0.1 M HCl. Mo and Ni showed only small effects of surface nitriding, while Fe exhibited higher rates of anodic kinetics. The mechanism by which surface nitrides modify the anodic kinetics of stainless steel is discussed.

INTRODUCTION

We have previously shown with X.P.S. that, during the anodic polarization of high nitrogen stainless steels, nitrogen is segregated to the alloy surface where it forms a relatively stable interstitial nitride phase enriched in Cr, Mo and Ni (1-4). We have also observed that N additions are responsible for enriching the passive film with Cr and Mo (5). Ni, however, appears to be absent from passive films formed on high and low nitrogen steels. The selective dissolution that leads to anodic segregation of nitrogen may to some extent mask the exact role of the surface nitride in modifying the anodic behavior of the steel. To circumvent this problem we have devised a simple technique to investigate the influence of surface nitrides on anodic behavior. Then, by comparing the influence of surface nitrides on the electrochemical behavior of pure metals and a series of stainless steels the mechanism(s) by which nitrogen modifies the anodic behavior of the stainless steels may be evaluated.

EXPERIMENTAL: MATERIALS AND EQUIPMENT

Pure specimens (99.99%) of Cr, Mo, Fe and Ni and types 304, 317LX, 904LX and AL6X stainless steels were used in this study. The composition of the steels are given in Table 1.

Table 1. Chemical compositions of the stainless
steels (wt%)

S.S.	C	Mn	P	S	Si	Ni	Cr	Mo	Cu	N
304	0.053	1.77	0.031	0.008	0.41	8.49	19.27	0.36	0.16	0.040
317LX	0.022	1.52	0.018	0.015	0.41	13.13	18.43	3.34	<0.01	0.055
904L	0.019	1.50	0.023	0.002	0.44	24.40	20.46	4.51	1.48	0.053
AL6X	0.028	1.60	0.023	0.004	0.33	23.86	20.65	6.27	<0.01	0.055

The specimens in coupon form (7x7x1 mm) were heat treated at 1100°C for 3 hours in an evacuated quartz tube and water quenched. These specimens were then mechanically polished up the grades to a 0.25 um diamond finish. They were then degreased ultrasonically in acetone, washed in propanol and finally mounted for electrochemical analysis.

The electrochemical equipment used in this study has been described elsewhere (6). The platinum auxiliary electrodes were accommodated in two separate compartments on opposite sides of the cell so that plating of Pt onto the working electrodes during nitrate reduction can be prevented.

The electron spectroscopy equipment used in this study is also described elsewhere (6). Two angles of photoelectron take-off have been employed in this work, 20° and 50° with respect to the sample surface. By comparing spectra at 20° and 50°, the species associated with the exterior surface of the passive film may be compared to the species associated with the interface region, respectively. However, for brevity we have only included 50° spectra. For reference the Au 4f 7/2 line was found to be 83.8 eV binding energy.

PROCEDURE FOR SURFACE NITRIDING AND POLARIZATION

Step 1. The specimens were cathodically pretreated in deaerated 0.1 M HCl for 15 minutes in order to reduce the air-formed oxide film.

Step 2. The electrolyte was removed under argon and totally refreshed in order to remove any species associated with the film debris.

Step 3. The specimens were then cathodically charged at -700 mV (vs.SCE) in the presence of 0.1 M HCl + 0.5 M NaNO3 with 750 mC cm^{-2}. In the case of Cr the charging potential was -930 mV (vs.SCE).

Step 4. The Cl$^-$/NO3$^-$solution was then removed under Argon and the cell was rinsed with 2000 ml of deaerated 0.1 M HCl.

Step 5. 0.1 M HCl solution was reintroduced to the cell. Anodic potentiodynamic polarization was then performed from the open circuit potential (O.C.P.) at a scan rate of 1 mV/sec.

Step 6. Control experiments were performed by following the above procedures without nitriding.

Step 7. The above procedures were repeated a minimum of three times for each of the specimens to insure reproducibility.

It should be noted that the above procedure evolved from preliminary electrochemical (7) and XPS (8) investigations.

XPS ANALYSIS

XPS analysis of the specimen surfaces was made: 1)   directly after surface nitriding treatment   2) following surface nitriding and anodic scanning to 0 mV (SCE) in 0.1M HCl. In each case the specimen was rinsed in distilled water and dried prior to transfer to the spectrometer. The sample washing, mounting and transfer to the spectrometer was performed under prepurified argon, in order to prevent atmospheric oxidation of the surface to be analyzed.

DETERMINATION OF THE EFFECTIVENESS OF SOLUTION
REFRESHMENT

By introducing controlled amounts of NaNO3 into the cell, we have attempted to   determine if the solution refreshment procedure was successful in removing most, if not all of the residual NaNO3 from the cell, and that oxygen contamination was prevented. Polarization curves for pure Cr, in figure 1A, demonstrate the effect of systematic additions of NaNO3 on the system. These results demonstrate that a significant concentration of nitrate is needed in order to affect the polarization behavior of Cr. This work indicated that the anodic polarization experiments reported in this paper following nitride surface treatment was performed in an environment essentially free from residual nitrate.
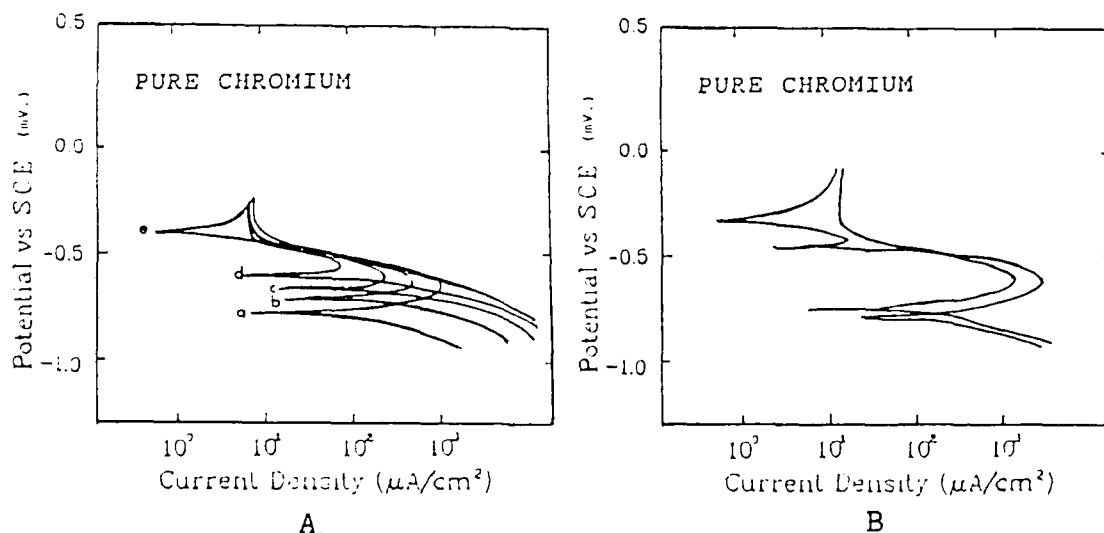

A   B

Fig. 1. Polarization curves for pure Cr. Fig.1A
        shows the effect of NaNO3 additions to
        0.1 M HCl. Curve a.) no nitrate b.) 0.1 M
        NaNO3   c.) 0.5 M NaNO3   d.) 1.0 M NaNO3
        e.) 1.5 M NaNO3 . Fig.1B shows the effect
        of oxygen on the system. Curve a.)   .02
        ppm oxygen b.) 7.15 ppm oxygen.

In other experiments, the oxygen content of the electrolyte was increased from 0.02 to 7.15 ppm as monitored with an oxygen sensing electrode (Orion Model 97-08). Figure 1B shows the effect of O_2 on the polarization behavior when added to the electrolyte. These preliminary experiments verify that in the presence of O_2, the formation of a cathodic loop is observed on the polarization curve. The absence of this loop following the deaeration procedure used throughout this work indicates that oxygen contamination is negligible.

RESULTS: PURE METALS

The N1s spectra for the pure metals which were cathodically pretreated in 0.5 M $NaNO_3$ + 0.1 M HCl yielded evidence, in each case, of surface nitride formation. The measured binding energies are given in table 2.

Table 2. Nitrogen binding energies after nitrate
treatment

Sample	Binding Energies (eV)	
	Nitride	NH3
Cr	396.5	399.6
Mo	397.0	399.9
Ni	397.4	399.7
Fe	396.6	399.8
304	396.9	399.7
317LX	396.9	399.9
904L	397.0	399.9
AL6X	397.0	399.8

The polarization curves for the pure metals, consisting of a single anodic scan from the O.C.P. are presented in figure 2.
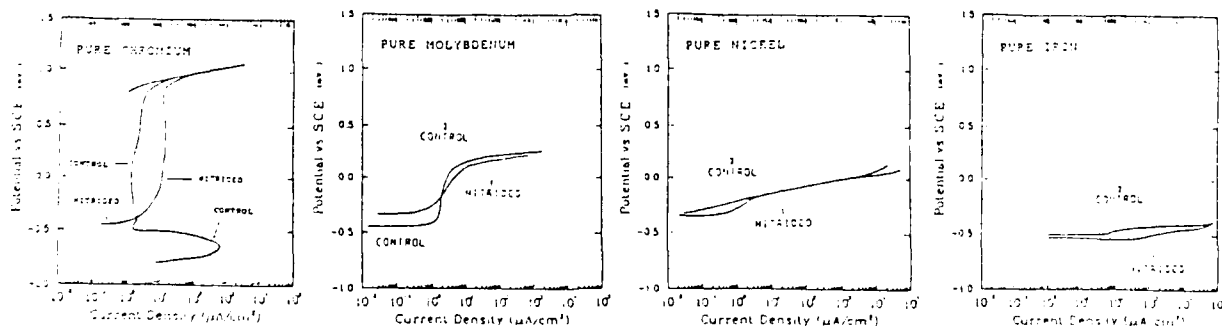

Fig. 2. Polarization curves for the pure metals
where the specimens were permitted to
float to the O.C.P. before polarization at

From figure 2, it is observed that the active corrosion of Cr is completely suppressed following surface nitriding. This observation includes a sizeable positive shift in the O.C.P. of the nitrided Cr as well as an expansion in the passive range of potentials. The passive current density was, however, increased. The polarization behavior of Fe indicated that the surface nitrided specimens exhibited an intensification of anodic activity when compared to the control. The influence of surface nitrides on the anodic activity of Ni was evidenced only by a smaller increase in anodic activity over a limited range of potentials above the O.C.P.. The nitrided Mo specimens exhibited a positive shift in O.C.P. and the anodic activity of nitrided Mo remained typical of the passive state.

STAINLESS STEELS

The N1s spectra for the stainless steel specimens which were cathodically pretreated in 0.5 M NaNO3 + 0.1 M HCl is presented in figure 3 and the measured binding energies are given in table 2.

1. Mo $3p^{3/2}$
2. Mo^{4+} $3p^{3/2}$
3. Nitride
4. Mo^{6+} $3p^{3/2}$
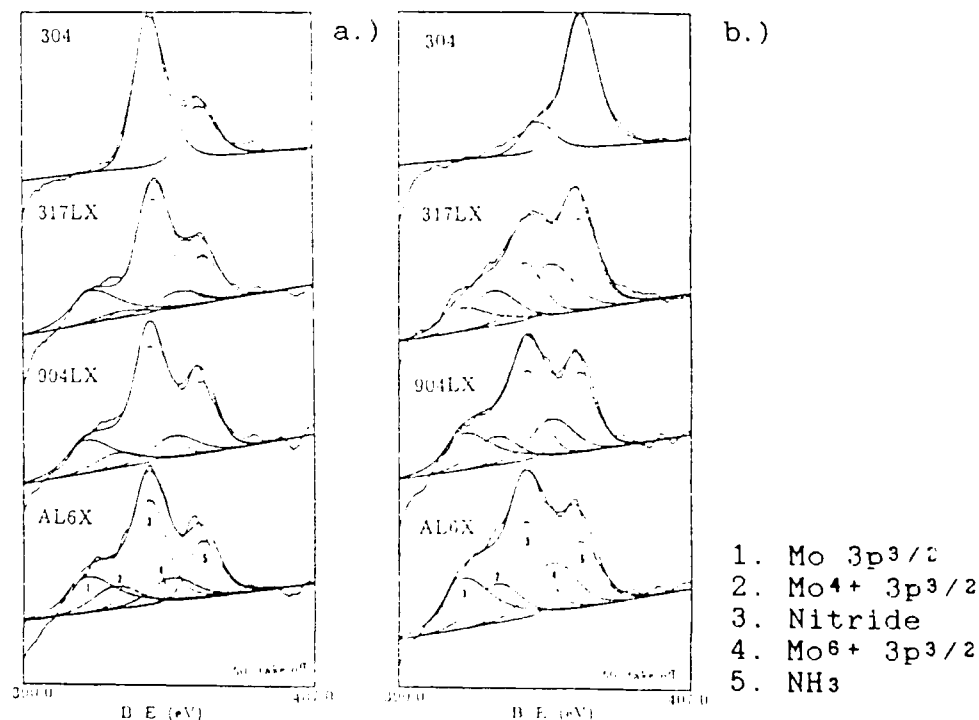5. NH_3

Fig. 3. N1s spectra for the stainless steels.
    3a. As nitrided
    3b. Following polarization from O.C.P. to 0 mV.

Strong N1s spectra associated with surface nitrides (ca.397.0 eV) is clearly indicated in figure 3a for each of the specimens, as are smaller but quite prominent NH_3 peaks (399.7). Both variable angle XPS and destructive depth profiling analysis indicated that the surface nitriding of 304 stainless steel resulted in only a shallow depth of nitriding, of the order of 1-3 monolayers. In figure 4, we see from the Cr $2p^{3/2}$ spectra that CrN (Cr $2p^{3/2}$=575.5 eV) appears to be present. However, the N1s binding energy value of 396.9 eV is 0.4 eV higher than for CrN, indicative of a mixed nitride (9). By contrast, the N1s spectra observed on the pure Cr sample is indicative of CrN.
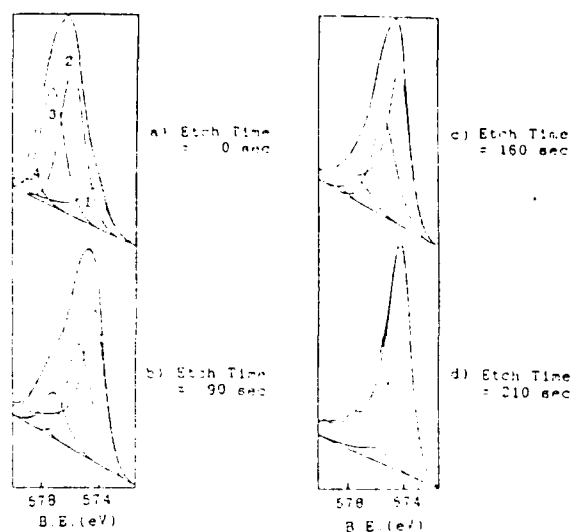
Fig.4. Cr 2p$^{3/2}$ spectra for 304 SS after nitride
treatment and Xe sputter etch (etch rate=
~4A/min, 2.5 kV, 16 uA, 10^{-8} torr). 1) Cr
(metal). 2) CrN. 3) Cr(OH)$_3$. 4) CrO$_4^{-2}$

The polarization curves for the stainless steels, consisting of a single
anodic scan from the O.C.P., are presented in figure 5 for both the
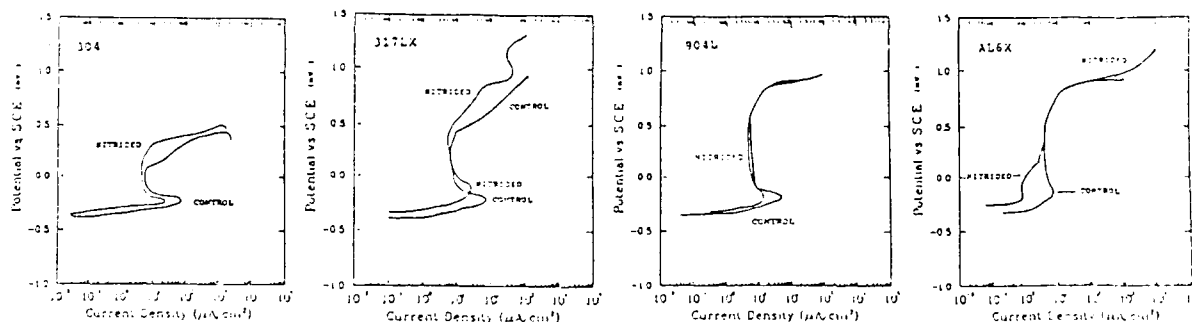nitrided and the control specimens.

Fig. 5. Polarization curves for the stainless
steels where the specimens were permitted
to float to the OCP before polarization

Anodic scanning from the O.C.P was performed after initial evidence
indicated that there was a loss of surface nitrogen following formation
of ammonia which occurs during the time taken to scan through the
cathodic region. Undoubtedly, this reaction is due to the protonation of
the surface nitrides by the highly electropositive H atoms derived from
the water molecules. The influence of the surface nitride on cathodic
kinetics will be discussed in a future publication.

The data indicates that each steel exhibits a distinctive drop in the
critical current density as a result of nitriding. The nitriding
treatment also induces an ennoblement of the corrosion potential as w·ll
as a reduction in the passive current density of each specimen. The
pitting potential is shown to be delayed for type 304 stainless steel,
and, the pitting of the m..ybdenum bearing 317LX S.S. was prevented
entirely by nitriding.

Referring to figure 3. it is apparent that on polarizing the specimens from O.C.P. to 0 mV, a distinct decline in each of the nitride peaks is evidenced as is a corresponding growth of the NH3 peak (399.7eV). This protonation of nitride to NH3 during the active range of dissolution is greatest for the 304 alloy attenuating progressively in correspondence to the increasing Cr and Mo content of the steels. Clearly absent is any evidence of an oxidized form of nitrogen such as NO2-or NO3-. This suggests that either the oxidized products are too soluble to remain on the surface or that the oxidation of N^{3-} species is, as reported by Pourbaix, kinetically unfavorable (10). This matter will be the focus of a separate study.

A useful technique for the determination from the anodic current density of the total amount of material oxidized requires calculation of the alloy equivalent weight (11). The resulting estimate provides for a comparison of the degree of nitride retention of the different alloys. Using this procedure, we calculated the number of monolayers of metal removed from both the pure metals and the stainless steels during the anodic scan from OCP to 0 mV. The data for the pure metals and for the stainless steels, listing the pertinent electrochemical parameters and the oxidized masses is presented in table 3. The valency was corrected with change of electrode potential.

Table 3. Results of the oxidized mass
calculations.

SPECIMEN	POLARIZATION OCP TO 0 (mV,SCE)	CALCULATED ALLOY EQ.WT. (g/mol.)	CHARGE (uC/cm2)	OXIDIZED MASS (monolayers)
304 con	-412 to 0	27.12	7450.47	22.53
304 nit	-307 to 0	27.12	6436.01	19.46
317LX con	-423 to 0	27.17	7953.88	24.91
317LX nit	-350 to 0	27.17	4541.58	13.61
904L con	-359 to 0	26.90	5712.86	16.38
904L nit	-332 to 0	26.90	3170.35	9.10
AL6X con	-325 to 0	27.14	1552.62	4.52
AL6X nit	-261 to 0	27.14	207.00	0.59
Cr con	-790 to 0	-	86061.71	178.96
Cr nit	-445 to 0	-	2975.87	6.19
Mo con	-450 to 0	-	791.38	1.65
Mo nit	-300 to 0	-	642.33	1.34
Fe con	-527 to 0	-	7.97×10^7	2.48×10^5
Fe nit	-552 to 0	-	10.38×10^7	3.24×10^5
Ni con	-327 to 0	-	72539.25	223.14
Ni nit	-351 to 0	-	76225.29	237.76

Briefly summarizing, the surface nitrided specimens of Cr, Mo, and each of the steels demonstrate distinctive reductions in the quantity of mass oxidized when compared to the control specimens polarized in the same 0.1 M HCl solution. The data shows an almost thirty-fold reduction in the number of monolayers of oxidized Cr following the application of a surface nitride compared to Mo which exhibited only a small decrease in anodic activity. The nitrided stainless steel specimens also show a decline in the number of oxidized monolayers of metal, with the oxidation values ranging from a two-fold reduction for 904L to an almost eight-fold reduction in oxidized mass for AL6X. This clearly indicates the combined influence of N and Mo on the active dissolution rate. Fe demonstrated a significant increase in the number of monolayers of metal oxidized following nitriding.

DISCUSSION

In considering the effect of surface nitriding of pure metals we note that passivity is only promoted in the case of Cr and Mo. It is tempting to assume that the highly covalent nature of the transition metal nitrides is responsible for sufficiently high bond strengths that the activation energy for dissolution is increased. However, Cr and Mo nitrides are relatively unstable, both exhibiting lower melting points than the elements (12). In the case of Fe and Ni nitrided samples, which showed no passive behavior, the stability of the nitrides are even lower than for Cr and Mo, and their active behavior was somewhat enhanced. The stability of transition metal nitrides are generally found to diminish both across the period and from 3d to 5d. Thus, the most stable nitride would be expected to be CrN. The remarkable reduction in active dissolution exhibited by the nitrided Cr samples, must therefore be related to the suppression of Cr^{2+} in favor of Cr^{3+} essential to passive film formation. It would appear that formation of CrN at high cathodic overpotentials as an intermediate step in NH_3 formation or perhaps as a direct chemical interaction of Cr with adsorbed NH_3 thus generates a surface phase rich in Cr^{3+} species covalently bound with nitrogen. The nitride thus acts as a precursor to the formation of the oxide passive film, with the following interfacial reaction taking place:-

$$2 CrN + 3 H_2O_{ads} \longrightarrow Cr_2O_3 + 2 NH_3 \text{ (ligands)} \qquad (1)$$
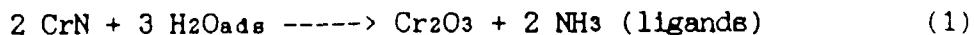
The stainless steels when nitrided show that the active nose is not entirely suppressed although it is reduced, and most effectively with increase of Mo content. Here we must take into consideration the fact that Cr, Mo and Ni, as we have reported previously, tend to become enriched in the nitride phase, due to selective dissolution of Fe (5). In steels containing only a trace of nitrogen, enrichment of the alloying elements is also observed, but the degree of enrichment of Cr and Mo is usually smaller (6). Of particular note is the fact that Ni rarely is observed in the passive films of N or non-nitrogen bearing stainless steels (5).

The alloy surface enrichment of Ni along with Cr and Mo raises the possibility of strong Cr-Ni or Mo-Ni interaction to form intermetallic compounds. Intermetallic compound formation, as a first stage in

passivatior, has previously been suggested by Olefjord et al. (13). Of relevance to the nitriding of stainless steels is the fact that a strong intermetallic interaction by Cr and Mo (both hypoelectronic d-metals) with Ni (hyperelectronic d-metal) in accordance with Brewer's model (14) may also provide the basis for nitride formation between several elements. Jack (15) has recently pointed out that while Mo and Ni nitrides are relatively unstable, mixed metal nitrides of Mo and Ni such as Ni_2Mo_3N are highly stable exhibiting strong lattice bonding. Hence, it is apparent that while nitriding Ni does not result in anodic inhibition, it would appear that in the alloy case, conditions favor the formation of a strongly bonded quarternary interstitial nitride which may act as a kinetic barrier, and which, in turn can support a passive film enriched with Cr and Mo. Such a duplex kinetic barrier is therefore envisaged as responsible for the enhanced corrosion resistance afforded stainless steel upon nitrogen alloying. Evidence for the effectiveness of the alloy nitride phase as a kinetic barrier is seen in the case of 304 ss in which after the oxidation of 40 monolayers of steel, a surface nitride is still observed which separates the metal phase from the electrolyte, in the extensive active range, and the passive film and the metal in the passive range of potentials. Furthermore, the nitride phase may be responsible for aiding repassivation of pit nucleii by (a) stifling active dissolution (b) decreasing local acidity by formation of ammonium ions and (c) providing a rich supply of Cr and Mo for oxide film formation.

SUMMARY

By studying the anodic behavior of surface nitride phases formed on pure metals and stainless steels and by comparison with our previous work on high N stainless steels we have determined the following:-

(1) That both high N and surface nitrided stainless steel appear to passivate by formation of a duplex kinetic barrier consisting of an outer oxide-based film and an interfacial interstitial nitride phase enriched with Cr and Ni or Cr, Mo, and Ni.

(2) Nitriding appears to enhance the anodic activity of Fe. Nitriding or N alloying of stainless steels results in enhanced selective dissolution of Fe.

(3) The nitride formed on Ni produced no beneficial effect on anodic kinetics, but it appears that Ni is an important component to a more protective mixed nitride phase. This may be due to promotion of strong intermetallic bonding with Mo and Cr.

(4) It is proposed that Mo is responsible for producing a more stable interfacial intermetallic compound between Cr and Ni in low nitrogen steels and a more stable mixed interfacial nitride in high nitrogen steels due to the formation of stronger Mo-Ni bonds compared to Cr-Ni. In both cases, Mo lowers the rate of active dissolution.

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